

FLOTATION STUDIES OF SULPHUR ORE FROM BATAL DEPOSITS, KOH-I-SULTAN BALOCHISTAN

M.A. QAZI, SAQIB AHMAD, MEHDI HASSAN, I.H. KHAN AND SHAFIQ ANWAR

PCSIR Quetta Laboratories, Quetta, Pakistan

(Received March 1, 1992; revised July 21, 1993)

Elemental sulphur occurs in the volcanic deposits of Batal area in Koh-i-Sultan. The sulphur content in the ore varies from 17 to over 50%. Sulphur particles upto 80%, could be liberated from the associated gangue at 44-60 mesh (B.S.S.). The composite ore sample averaging 32.2% sulphur was crushed, ground and floated. Flotation tests on the composite Batal sulphur ore ground to about 44 mesh size showed a significant response to kerosine as collector and polyglycol and MIBC as frothers. Effect of different variables such as particle size, pulp density, pH, reagents, conditioning time and impeller speed was studied on the flotation of sulphur. Final concentrate containing about 80% sulphur at 75.9% recovery was obtained after three cleaning stages. The flotation conditions found optimum were particle size 60 mesh (80% passing), at pH 2.5 and impeller speed 1000-1200 rpm. The reagent used were 0.3 kg/t kerosine, 0.2 kg/t MIBC and 2.0 kg/t sodium pyrophosphate.

Key words: Flotation, Batal sulphur deposits.

Introduction

The sulphur deposits in Pakistan occur in Batal and Miri area at Koh-i-Sultan in the province of Balochistan. The ore deposits in these areas were estimated at 170,000 tonnes of over 25% sulphur and over 250,000 tonnes of about 20% sulphur [1]. The Koh-i-Sultan sulphur deposits lie between latitude 29° to 29° 15' 36" and longitude 62° [2,3] in Chagai district Quetta division. The deposits are 37 km towards north of Nokundi and about 650 km to the west of Quetta. The deposits are connected with Nokundi by a jeepable fair weather road.

Narayanan [4] tested froth flotation of sulphur ore samples from Koh-i-Sultan. In the rougher flotation 0.16 kg/t creosote and 2.7 kg/t sodium silicated was used while in cleaner flotation 0.08 kg/t creosote was used. In a single cleaning operation a concentrate assaying 70 percent sulphur was obtained. The author considered the flotation method to be unsuccessful because of contamination of ore with amorphous silica.

Gohar *et al.* [5] and Qazi *et al.* [6] have worked on the beneficiation of Balochistan Sulphur Refinery rejects, containing about 22% sulphur, using flotation method. They have reported that grades of concentrate containing over 81% sulphur at 70 and 82% recoveries respectively were obtained. Bench scale studies on Batal ore indicated that the ore was amenable to beneficiation by flotation.

Three ore samples from Batal area were collected from a vertical section, designated as KS-IA, KS-IB and KS-IC, for the investigation.

The ore samples were irregularly thinly bedded, consolidated and associated with very fine ash that is the host rock for

sulphur. The rock apparently has been intensely altered and bleached by sulphuric action. The gangue materials were tuff, clay anhydrite etc., although there is about 2.5 percent water soluble aluminium sulphate, formed by leaching of alumina-silicates [7]. The densities of the ore samples ranged from 1.86 to 2.06 gram/cm³.

Materials and Methods

Chemical analyses of the sulphur ore, oven dried at 150°, were conducted on samples KS-IA, KS-IB, KS-IC and a composite sample made by mixing equal weights of the three sulphur ore samples. Sulphur determination was done using carbon disulphide extraction methods [8,9]. For other elemental analysis, conventional wet chemical analytical methods, spectrophotometer, atomic absorption spectrophotometer and optical spectroscope were used (Table-1).

It may be seen that the sulphur content in the ore samples varied from 17.7% to 50.21%. The major impurities were silica calcium and sulphate ions. Among the minor impurities, selenium, mercury and arsenic were below 10 ppm (acceptable limit).

Liberation study on the individual and the composite sulphur ore sample was conducted by particle count method using an optical microscopic. In each test, the dried ore sample passing 6.35 mm was ground in a one litre capacity ceramic pebble mill for 5 min, in dry or wet state (40 percent pulp density).

Grinding study was carried out on composite ore sample. The ore was crushed through Karl Kolb (10 x 7.5 cm) laboratory jaw crusher and then crusher and then through Denver crushing rolls (25 cm) to a size 100% passing 6.35 mm. The

roll product (100 g) was ground in a 5 litre capacity ceramic pebble mill running at 40 rpm in wet state maintaining 40 percent solids in the pulp.

Portions of pulp were drawn at 5, 10 and 15 min intervals and subjected to wet sizing analysis. The individual size fractions were dried and weighed.

Flotation study on the composite ore sample was carried out using Denver D₁₂ laboratory flotation machines. Stainless steel cells of capacities 5 litre to 500 ml were used in roughing, cleaning and recleaning operations.

The composite ore for flotation study was wet ground for 5–6 min in a ceramic pebble mill to get 80% particles passing 44 mesh (liberation size). Grinding time was changed in order to get size fractions 80 percent passing 22, 30, 40, 60 and 100 mesh. Pulp densities of 10, 15, 20 and 25% solids was maintained to determine the optimum value of pulp density. The particle size during this series of tests was kept at 80% passing 30 mesh.

The effect of reagents on the flotation of Batal sulphur was studied using kerosine as collector, polyglycol-400 (Cyan-

amid) and MIBC as frothers and sodium phosphate as depressant for gypsum. Amount of kerosine was varied from 0.1 to 0.5kg/t, amount of frothers were changed from 0.1 to 0.4kg/t. The conditioning time was changed from 2 to 10 min. Froth was collected at one min intervals. It was dried, weighed and analysed for sulphur.

Effect of pH was studied using 1000 ml pulp having particle size 80% passing 30 mesh, at 20% solids. The pH was changed from 2.5 to 9.5.

In the cleaner flotation circuit, the rougher concentrate obtained, using optimum conditions, was ground to a product 80% passing 60 mesh. A pulp density of 10% solid was used and the pH was kept at natural value (6.0-6.2). The reagent requirement at the cleaning stage was nominal. The first cleaning concentrate was recleaned in two subsequent steps.

Flotation concentrates were dewatered using Denver bench pressure filter. The moist concentrates were oven dried at 70°.

Results and Discussion

The sulphur ore KS-IA a tendency to disintegrate on wet grinding. This may be due to weak cementing of sulphur particles with tuff and clay. It may be seen from Table-2 that on wet grinding, over 83% sulphur particles were liberated at 30 mesh, while in dry grinding operation such an order of liberation could only be achieved between 60 and 100 mesh size.

The sulphur sample KS-IB was rather hard and massive although it behaved almost similarly as KS-IA. Sulphur particles could be liberated upto 80% from gangue, between 44 and 60 mesh on wet grinding.

The ore sample KS-IC was slightly lumpy but had appreciable amount of fines. The ore was somewhat resistant to grinding. There was no significant difference in the liberation on dry and wet grinding. About 80% sulphur particles were liberated at 60 mesh.

Liberation study on the composite sample showed that about 80% sulphur particles were released from the associated gangue at 60 mesh size. At 100 mesh about 90% sulphur particles were liberated. It was concluded that grinding be-

TABLE 1. CHEMICAL ANALYSIS OF SULPHUR ORES FROM BATAL.

Constituents	KS-IA	KS-IB	KS-IC	Composite
S (Wt.%)	17.7	50.2	33.0	32.2
SiO ₂	51.0	35.7	51.1	46.8
Fe ₂ O ₃	00.5	00.9	02.7	01.5
Al ₂ O ₃	02.6	02.2	02.9	02.8
CaO	09.9	02.5	01.9	04.9
MgO	00.1	00.1	00.2	00.1
Na ₂ O	00.03	00.2	00.2	00.1
K ₂ O	00.02	00.05	00.09	00.05
Cl (ppm)	290	215	260	254
Ni	42	60	48	53
Se	<10	<10	<10	<10
Cd	740	810	925	820
Pb	10	14	12	10
Hg	<1	<1	<1	<1
As	<10	<10	<10	<10

TABLE 2. LIBERATION STUDY OF BATAL ORE SAMPLES ON DRY AND WET GRINDING.

Size mesh (B.S.S.)	Dry Grinding								Wet Grinding							
	KS-IA		KS-IB		KS-IC		Composite		KS-IA		KS-IB		KS-IC		Composite	
	Cum.wt.% Retained	Free S Vol.%	Cum.wt.% Retained	Free S Vol.%	Cum.wt.% Retained	Free S Vol.%	Cum.wt.% Retained	Free S Vol.%	Cum.wt.% Retained	Free S Vol.%	Cum.wt.% Retained	Free S Vol.%	Cum.wt.% Retained	Free S Vol.%	Cum.wt.% Retained	Free S Vol.%
+ 30	18.7	53.6	17.3	47.3	17.8	57.1	24.3	55.3	04.0	83.7	30.9	74.0	05.4	69.5	17.3	72.3
44	39.3	64.0	34.3	68.4	35.4	65.9	35.4	66.1	08.3	86.8	39.9	85.7	17.8	73.2	32.4	81.9
60	62.5	77.9	52.6	87.2	56.0	78.2	55.4	79.5	17.6	88.9	48.0	90.5	30.8	81.9	46.2	87.1
100	74.4	86.6	62.4	92.7	70.3	85.6	67.3	88.1	35.2	93.2	57.4	94.1	46.4	90.6	61.9	92.6
150	95.0	90.4	94.5	94.9	84.9	91.3	87.9	96.2	41.0	98.3	60.3	98.7	50.4	98.0	70.3	98.3
150	100.0	94.5	100.0	99.2	100.0	99.4	100.0	98.6	100.0	99.9	100.0	99.8	100.0	99.9	100.0	99.6

yond 100 mesh was not beneficial. In actual practice, grinding to below 44 mesh was considered sufficient for rougher flotation.

Grinding study. Wet grinding of composite Batal sulphur ore showed that about 80% of 44 mesh particles (liberation size) might be obtained on grinding for 5–6 min., whereas about 90% particles passing 44 mesh could be obtained on grinding for 12–13 mins. On increasing the grinding time beyond 6 mins. however, excessive fines were generated. These fines, which were predominantly those of gangue minerals reported in the froth during flotation, resulting in lowering the grade.

Flotation study. Preliminary flotation tests on composite Batal sulphur ore ground to liberation size was conducted in order to determine suitable conditions. A systematic study was carried out to determine the effect of particle size, pulp density, pH, reagents, conditioning time and impeller speed on the flotation of sulphur.

Particle size had a significant effect on the grade and recovery of sulphur as it was reduced from 22 mesh to 60 mesh in the rougher feed. On reducing the particle size further to 100 mesh the grade, as well as, recovery of sulphur, was reduced. Microscopic examination of rougher concentrate showed that fine particles of gypsum co-floated along with sulphur. it was concluded that grinding the Batal ore beyond 30 mesh was not yielding particularly higher grade or recovery of sulphur, whereas the power consumption on finer grinding would be excessive. In the subsequent flotation trials, particle size of 80-85% passing 30 mesh was maintained.

The effect of pulp density at lower contents of solids (10–15%) did not show noteworthy difference in the grade or recovery. At 20% solids and beyond, the grade and recovery showed a decline. It was decided to conduct further tests at 20% solids, at which a higher throughput may be handled, although at slight loss in the grade and recovery.

The increase in the pH from 2.5 to 9.5 had a positive effect on recovery which increased from 92 to 95% but the grade in the rougher flotation fell from 57.5% sulphur to 54.8. The natural pH of the pulp was 2.0–2.5, addition of lime was necessary to raise the pH. It was considered adequate to

conduct rougher flotation at natural pH and recover as much, sulphur values in the scavenger cell, as possible. This would reduced the cost of lime addition.

Sulphur is a naturally floating mineral, however, addition of kerosine as collector significantly improved the grade and recovery of sulphur. Addition of 0.1–0.5 kg/t kerosine improved the grade from 52.1 to 56.1% whereas, the recovery showed considerable improvement which was increased from 56.8 to 91.82%. It was, however, noticed that the increase in the grade and recovery beyond the collector dosage of 0.3 kg/t did not show any significant improvement.

The effect of frother on the flotation of Batal sulphur showed that the grade and recovery increased with an increase in the frother. A maximum recovery of 96% was achieved using 0.2 kg/t MIBC or 0.3 kg/t polyglycol-400. It was noted that MIBC yielded the same extent of grade and recovery at 33% less consumption as compared to polyglycol.

Effect of the addition of depressant for the gangue gypsum on the flotation of Batal composite sulphur ore was studied. Several preliminary trials using sodium silicate, tri-polyphosphate, sodium pyrophosphate etc. were used. It was found that sodium pyrophosphate gave better results. A dosage of 2.0 kg/t sodium pyrophosphate was adequate for depressing gypsum.

The conditioning time had a significant effect on grade and recovery of sulphur. It may be seen from Table-4 that the grade and recovery increased with increase in the conditioning time upto seventh minute. Beyond this the recovery was found to decrease, while the grade remained unchanged.

Effect of impeller speed indirectly affected the grade and recovery of sulphur. In a large capacity cell (5-8 litre) and at a pulp density of 20% solids or more, impeller speed below 1200 rpm did not provide sufficient mixing and aeration of the pulp. The surface layers remained almost undisturbed. It was found that at 1300-1500 rpm thorough mixing was achieved. In small cells, on the other hand (500 ml⁻¹ litre), impeller speed of 1000-1200 rpm was found sufficient. At pulp densities lower than 15% solids, impeller speed of 1000-1100 rpm was considered adequate.

While studying the effect of flotation time it was noticed

TABLE 3. EFFECT OF pH ON THE FLOTATION OF BATAL SULPHUR ORE.

	pH			
	2.5	4.5	7.00	9.5
Sulphur in feed (%)	32.1	32.0	31.7	31.5
R. Con. (% wt)	51.5	53.5	54.8	54.6
Grade (% S)	57.5	55.9	54.7	54.8
Recovery (% S)	92.3	93.4	94.6	95.0

TABLE 4. EFFECT OF CONDITIONING TIME ON THE FLOTATION OF BATAL SULPHUR.

	Conditioning Time (minute)			
	2	5	7	10
Sulphur in feed (%)	31.9	31.4	32.0	31.8
R. Con. (% wt)	47.5	51.1	52.9	51.1
R. Con. Grade (% S)	52.7	58.7	75.7	57.4
Recovery (% S)	78.4	94.7	95.4	92.2

that about 74% sulphur was recovered in the froth, during the first min of flotation. By third minute, over 96% sulphur was recovered. During further 2 mins of flotation only 2.5 sulphur was recovered (Table 5).

It may be concluded that the rougher concentrate may be collected up to 2 mins, whereas scavenger concentrate may be collected for the subsequent period of 3 mins. The overall grade of this scavenger concentrate would be over 15% sulphur. The grade of scavenger concentrate could be improved, however, on reducing this time to 1.5–2 mins.

TABLE 5. EFFECT OF FLOTATION TIME ON GRADE AND RECOVERY OF BATAL SULPHUR.

Product	Weight %	Grade % S	S. Distribution %	Recovery % S	Cum Grade %S	Cum Recovery %S
Head	100.0	32.1	32.1	100.0	32.1	100.0
1st min	39.2	60.7	23.8	74.1	60.7	74.1
2nd "	10.9	50.8	5.5	17.1	58.5	91.2
3rd "	6.9	25.1	1.7	5.3	54.4	96.5
4th "	7.5	9.2	0.7	2.2	49.1	98.7
5th "	1.7	4.3	0.1	0.3	48.0	99.0
Tails	31.4*	1.1	0.3	1.0	32.1	100.0

*Also contained 2.4 percent of the water soluble salts in the ore (e.g. aluminium sulphate).

TABLE 6. CLEANER CONCENTRATE OF BATAL SULPHUR ORE.

	Rougher	Cleaner
Particle size (80% passing) mesh	30	60
Pulp density (% solids)	20	10
pH	2.5	6.5
Impeller speed (rpm)	1000	1000
Reagents (kg/t)		
Kerosine	0.3	0.08
MIBC	0.2	Nil
Sod. pyrophosphate	2.0	2.00

Production	Weight %	Grade %S	Distribution %S	Recovery %S
Head	100.0	32.1	32.1	100.0
R. Con	54.6	56.7	30.9	96.3
R. Tails	45.4*	2.6	1.2	3.7
Cl. Con. I	42.0	65.9	27.6	86.0
Cl. Tails I	12.6	26.0	3.3	10.3
Cl. Con. II	32.9	75.0	24.9	77.6
Cl. Tails III	9.1	29.7	2.7	8.4
Cl. Con. III	30.4	80.1	24.3	75.7
Cl. Tails III	2.5	23.9	0.6	1.9

* Also contained water soluble (2.4%) aluminium sulphate in sulphur ore.

The rougher concentrate after three cleaning steps yielded a product containing about 80% sulphur. It may, however, be visualized (Table-6) that the cleaner tails I, II and III altogether corresponded to 24.2 weight percent and assayed about 27% sulphur. This is very near the feed grade to the rougher circuit. On recycling these tails, a higher recoveries may be expected.

Further R & D work on pilot-plant may be conducted on continuous basis in order to simulate the plant conditions and to calculate the materials balance.

Conclusion

The Batal sulphur ore contained variable amount of sulphur ranging from 17 to 55%. A composite ore sample was blended from three bulk ore samples assaying 32.2% sulphur. The amounts of objectionable elements such as Se, Hg, As, Cd, Pb, were within limits.

The ore was amenable to beneficiation using a flotation technique. The flotation parameters on which optimum grade and recoveries could be obtained were:

Grinding the ore to 80% passing 30 mesh (B.S.S) in roughing and to 60 mesh in cleaner flotation.

Maintaining a pulp density 20% solids during rougher flotation and 10% solids during cleaning.

Natural pH of 2-2.5 was used during roughing and 6.0-6.5 during cleaning.

The impeller speed found adequate was 1300-1500 for 6-8 litre cells (Denver D12) and 1000-1200 for up to 2 litre cells.

The reagent consumption found suitable was 0.3 kg/t kerosine, 0.2kg/t MIBC 2.0 kg/t sodium pyrophosphate. Very little additional reagents were required for cleaning. However, 2.0 kg/t sodium pyrophosphate was required at each cleaning step.

The concentrate grade after three cleaning steps was found to be about 80% sulphur over 75% recovery. The recovery, however, may possibly be enhanced by recirculation of cleaner tails.

References

1. M. Emerson, Evaluation of Sulphur in Balochistan UNIDO Sixth Mission Report (Pak/85/023).
2. A.M. Heron, *Directory of Economic Minerals of Pakistan*. (Geol. Sur. of Pakistan, 1955), Vol. 7th, Part 2.
3. W.M. Goldberger, Evaluation of the Commercial Recovery of Elemental Sulphur from Koh-i-Sultan Deposits in Balochistan (UNDP) Dec. (1988).
4. P.I.A. Nayayanan, *Trans. Min. Geol. and Metallur. Inst. India*, 41(2), 129 (1946).
5. R.A.K. Gohar, Hussain and N. Sheikh, *Pak. j. sci. ind. res.*, 32, 709 (1989).
6. M.A. Qazi *et. al.*, Laboratory Testing of Koh-i-Sultan

Sulphur Ore PCSIR Report Feb. (1991).
 7. M.I. Ahmad, *Volcanoes and Sulphur of Western Balochistan* (Geol. Sur. Pakistan, 1951), Vol. IV, Part 3.
 8. N.H. Furman, *Standard Methods of Chemical Analysis*

(Report Krieges Publ. Co., New York, 1975), Vol. I, 6th ed., pp. 1030-31.
 9. W.N. Tuller, *The Sulphur Data Book* (McGraw Hill Book Co. Inc., 1954), pp. 98-105.

Department of Chemistry, University of Rajshahi, Rajshahi, Bangladesh

(Received November 18, 1992; revised June 28, 1993)

The EI mass spectrum of the mixed ligand quadruply bonded molybdenum complexes $Mo_2(O_2CCH_3)_2(2PF_3)_2$ and $Mo_2(O_2CCH_3)_2(2PF_3)_2$ show fragments which are observed in the mass spectrum of the parent nonbonded compounds. The fragmentation of $Mo_2(O_2CCH_3)_2(2PF_3)_2$ is similar to that of the parent compound $Mo_2(O_2CCH_3)_2$. $Mo_2(O_2CCH_3)_2(2PF_3)_2$ on the other hand show fragments that is not observed in the mass spectrum of the parent compound. The acetate bridged mixed ligand complex show fragments containing one molybdenum atom resulting from the cleavage of the metal-metal bond, a process not observed in the mass spectrum of the parent compound.

Key words: Mass spectrum, Molybdenum complex, Dithia-phosphinate acetate ligands.

Experimental

The mixed ligand molybdenum complexes $Mo_2(O_2CCH_3)_2(2PF_3)_2$ and $Mo_2(O_2CCH_3)_2(2PF_3)_2$ by the stoichiometric reaction of Mo_2F_{10} as appears in literature [10]. The mass spectra of the complexes were obtained with a VG70E or mass spectrometer. A 70 eV ionization voltage was used for ionizing the samples. Samples were introduced into the ionization chamber via direct introductory probe.

Results and Discussion

$Mo_2(O_2CCH_3)_2(2PF_3)_2$. The EI mass spectrum of this compound shows the molecular ion at m/z 684 which is the base peak in the fact that the cluster of peaks at 684 is due to the composition $Mo_2(O_2CCH_3)_2(2PF_3)_2$ is confirmed by theoretically calculating the molecular ion peak pattern (the number and intensity of peaks). The experimental spectrum for the molecular ion in excellent agreement with that of the calculated spectrum.

Like the parent compound $Mo_2(O_2CCH_3)_2$ from which the compound under study was prepared, loss of a fluorine atom occurs to give a fragment of m/z 665. Loss of a CF_3CO_2 group from the molecular ion gives an ion at m/z 290; this ion was also observed in the mass spectrum [11] of $Mo_2(O_2CCH_3)_2$. Loss of CF_3 or PF_3 (vs m/z 69) from the molecular ion gives only a low-abundance ion at m/z 615. The ion observed at m/z 437 probably represents in part the loss of PF_3 and PF_2 fragments. This ion also appears in the spectrum of $Mo_2(O_2CCH_3)_2$ but with lower relative intensity than that observed for mixed ligand compounds. The peak at m/z 192, assignable to $MoO_2F_2^+$, is also observed here like that of the parent compound. A series of low mass ions at m/z 165, 146 and 130 are observed all of which show isotopic cluster characteristic of one molybdenum. They may be assigned to Mo_2^+ for

Introduction

Molybdenum exhibits a large number of oxidation states among which the +3 state is especially important since the metal ions in this oxidation state form complexes containing multiple metal-metal bond [1-5]. The small metal-metal bond distance in such compounds as $K_2Mo_2Cl_6$ (2.139 Å) [6], compared to single-bond distances, supports the view of the multiple nature of the Mo-Mo bond formed by the overlap of appropriate metal d-orbitals. Characterization of compounds containing multiple Mo-Mo bonds is done mainly by X-ray crystallography, IR, Raman Spectroscopy, EPR and NMR methods [7,8]. For some molybdenum complexes good elemental analysis results were not obtained although other methods conclusively characterized those compounds [9,10]. In such cases where a good crystal is not obtainable for crystal structure determination and the result of elemental analysis is not excellent, the mass spectral data may offer an insight into the composition and structural features of those compounds.

There has been very few reports [11,12] on the mass spectra of complexes containing Mo-Mo units. The molecular ion peak and well separated peaks for fragments help in characterizing these compounds from their mass spectra. The presence of a large number of isotopes of Mo atoms with a natural abundance lying between 9 and 26, results in a 13 line peak pattern for fragments containing Mo-Mo units. Although this complicates the spectrum, the isotopic combination can be used to characterize the fragments having Mo-Mo units and single atom Mo. In this paper the mass spectra of two newly synthesized quadruply bonded molybdenum complexes, whose crystals were not obtainable, are reported along with a comparison of the mass spectra of their parent compounds.